

St. Joseph's Journal of Humanities and Science ISSN: 2347-5331

http://sjctnc.edu.in/6107-2/

# Synthesis and Enhanced Photo Degradation on Copper Ferrite Nano Particles

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[85N: 2347-5331]

St. Joseph's Journal of HUMANITIES AND SCIENCE

# ABSTRACT

The Co-precipitation method was effectively used in this study to create copper ferrite. It has positive surface because the potential hydrogen (pH) was held constant at 11. The temperature for annealing was set at 600°C for the synthesis of copper ferrite. The outcomes of the photocatalytic activity showed how to remove organic pollutants from wastewater.

**Keywords:** Co-precipitation method; Annealing; organic pollutants; wastewater; copper ferrite, photocatalytic activity.

# **INTRODUCTION**

The Mixed ceramic Ferrite has been examined in the current years by many experts (researchers) by reason of their distinctive structural, optical, morphological along with magnetic properties. These materials are reasonable interest for an extensive multiplicity of applications like highspeed digital tapes, optoelectronics, isolators, phase shifters, electrochemical technology, radio frequency circuits, great quality filters and transformer cores [1]. Iron oxide mixed ferrite materials can be integrated using different techniques viz. hydrothermal [2, 3], sol-gel [4] auto combustion [5, 6] and co-precipitation [7]. One of the quick and affordable methods for creating multiple aspects of mixed ferrites is co-precipitation. So, one of the fundamental paths to success created by various ferrites is the co-precipitation technique. A prominent ferromagnetic material with an inverse spinel structure is nickel ferrite [8]. This compound is characterized by the formula (Fe<sup>2</sup>+) (Ni<sup>2</sup>+Fe<sup>3</sup>+) O4, whereas half of the iron atoms occupy the

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tetrahedral (A) sites and the other half, together with magnetic atoms, occupy the octahedral (B) sites. The octahedral site (B site) is owned by Ni<sup>2+</sup> and Fe<sup>3+</sup> nanoparticles in this structure, whereas the tetrahedral site (A site) is entirely occupied by  $Fe^{3+}[9, 10]$ . The grain parameter's elongation is judged to follow Vegard's law as the larger radii are replaced with smaller radii [11]. It shows that the antiparallel spins between Fe<sup>3+</sup> in the tetrahedral position and Ni2+ in the octahedral position is the origin of ferrimagnetisms. The dynamic development of the surface impact predominates the reduction in particle size. Misperception in the grain symmetry that exhibits anisotropy is caused by a modification of the structural and ionic characteristics near and at the particle's surface. Many of the features of the particles, such as superparamagnetism and the cubic spinel structure of Ni-Cu ferrites are due to their single domain nature [12, 13]. Due to their excellent qualities, the magnetic ferrite Polyvinylpyrrolidone (PVP) composites are a particularly attractive option for this kind of application. Due to its responsiveness, modestness, nontoxicity, hydrophilicity, and biocompatibility, polyvinylpyrrolidone (PVP) offers a variety of potential biomedical and packaging uses [14]. In the current study, we investigate the consequences of variations in the Cu2+ arrangement used to combine Ni<sub>1</sub>, Cu<sub>2</sub>Fe<sub>2</sub>O<sub>4</sub> nanoparticles at the level of size, shape, and magnetic characteristics. Co-precipitation is a straightforward approach that we used to include copper-substituted nickel ferrites nanoparticles. A typical, conventional substrate shows photocatalytic activity when nickel ferrite nanoparticles are analyzed. Particularly, ferrite nanoparticles made of Ni, Mg, Co, Zn, and Cu produced greater catalytic activity than iron oxide  $Fe_3O_4$  [15, 16]. The degradation of methylene blue was evaluated to determine NiFe<sub>2</sub>O<sub>4</sub>'s photocatalytic activity, and NiFe<sub>2</sub>O<sub>4</sub> had the highest photocatalytic activity [17]. The greatly increased photocatalytic efficiency is ascribed to the narrowing of the band gap in nickel ferrite and the decreased recombination of photoinduced electron-hole pairs with increasing  $Cu^{2+}$  concentration [18]. For significance of reduction in size can be discussed below:

- 1. Modify in domain structure (Single domain structure)
- 2. Modify in the mechanism of magnetization

(Superparamagnetism; the free electron position g = 2.0023)[19]

- Modify in property (Coercivity, Retentivity = 0)
- 4. Performance (photocatalytic treatment)

Ferrites are typically used in composite systems because they are good at separating the electronhole pairs (radicals) produced by UV-irradiation [20].

$$\begin{split} \mathrm{MFe}_{2}\mathrm{O}_{4} + \mathrm{hv} &\rightarrow \mathrm{M}^{2} + \mathrm{Fe}_{2}\mathrm{O}_{4} \left[\mathrm{h}^{+} \left(\mathrm{VB}\right) + \mathrm{e}^{-}(\mathrm{CB})\right] \\ \mathrm{MFe}_{2}\mathrm{O}_{4} \left(\mathrm{h}^{+}\right) + \mathrm{OH}^{-} \rightarrow \mathrm{MFe}_{2}\mathrm{O}_{4} + \mathrm{OH}^{-} \\ \mathrm{O}^{4} + \mathrm{e}^{-} &\rightarrow *\mathrm{O}^{4} \\ \mathrm{h}^{+} + \mathrm{OH}^{-} &\rightarrow *\mathrm{OH} \\ \mathrm{h}^{+} + \mathrm{H}_{2}\mathrm{O} &\rightarrow \mathrm{H}^{+} + *\mathrm{OH}^{-} \\ &*\mathrm{OH}^{-} + \mathrm{Methylene \ orange} \\ (\mathrm{MO-C}_{14}\mathrm{H}_{14}\mathrm{N}_{3}\mathrm{NaO}_{3}\mathrm{S}) \ \mathrm{dye} \rightarrow \mathrm{Degradation} \\ \mathrm{products} \\ &*\mathrm{O}^{4} + \mathrm{Methylene \ orange} \ (\mathrm{MO}) \ \mathrm{dye} \\ &\rightarrow \mathrm{Degradation \ products} \end{split}$$

Where, the divalent metal ions  $M^{2+}Fe_2O_4$  are shown. The dye must first be adsorbed onto the sample  $M^{2+}Fe_2O_4$  nanostructure surface. Electronhole (e- h+) pairs are produced in  $M^{2+}Fe_2O_4$ nanostructures that have dye adsorbed on them when they are exposed to sunlight. Superoxide anion radicals (\*O<sup>2-</sup>) are created when oxygen molecules adsorbed on  $M^{2+}Fe_2O_4$  contact with the photogenerated electrons in the conduction band of h<sup>+</sup>. Surface hydroxyl groups react with holes created in the valence band of  $M^{2+}Fe_2O_4$  to create highly reactive hydroxyl radicals (\*OH) [21]. These photogenerated holes may cause the water molecules in the aqueous solution to dissociate, resulting in radicals. The choice of methylene orange (MO) dye is due to the highly reactive hydroxyl radicals (\*OH) and superoxide radicals (\*O<sup>2-</sup>) that can react with light degradation [21]. Over a wide absorption range, nickel and iron maintained a usually modest absorbance. As a result, the  $M^{2+}Fe_{2}O_{4}$  samples appear to absorb more light than Cobalt ferrites and as a result, have improved photocatalytic performance. For MO - $M^{2+}Fe_{2}O_{4}$  solution, the percentage deterioration rises sharply with the passage of time. Because of the method that various articles that were published for their investigation of NiFe<sub>2</sub>O<sub>4</sub>'s photocatalytic activity in the degradation of methylene blue under the influence of visible light were conducted. The size of the zinc ferrite was less than 15 nm, according to research by XU Shihon et al. They also reported that the nano size is advantageous for treating wastewater, as shown by photocatalytic analysis [22]. The organic pollutant is removed under UV- irradiation using both oxalic acid and H<sub>2</sub>O<sub>2</sub> was reported by Shou-Qing Liu et al [17] by using GO–NiFe<sub>2</sub>O<sub>4</sub> nanomaterials. The graphene plays an imperative role of photocatalytic process in the absorption of visible light, BO XIAO et al and also reported GO-NiFe<sub>2</sub>O<sub>4</sub> species enables to speed the degradation of organic pollutants in the presence of both oxalic acids under visible light irradiation whereas NiFe<sub>2</sub>O<sub>4</sub> species fails under similar conditions [23]. MB concentration has the significant effect on the rate of photodegradation and this was determined for NiFe<sub>2</sub>O<sub>4</sub> ferrites, its potential application for photo-Fenton like degradation of organic pollutants from wastewater, Rimi Sharma et al [24]. MO over Ni<sub>0.6</sub>Cu<sub>0.4</sub> Fe<sub>2</sub>O<sub>4</sub>: TiO<sub>2</sub> under solar light irradiation, the followings facts were considered:

- The layered structure, high surface area, and good sorption ability of Ni<sub>0.6</sub>Cu<sub>0.4</sub> Fe<sub>2</sub>O<sub>4</sub>: TiO<sub>2</sub> [25].
- The electron hole pair mechanism in MO octahedral/tetrahedral and the acceptance of photo holes by surface hydroxyl groups [21].

- 3) The band-gap energy of  $Ni_{0.6}Cu_{0.4}$  Fe<sub>2</sub>O<sub>4</sub>: TiO<sub>2</sub> and the electron-hole recombination factor [18].
- 4) The beneficial effects of interlayer TiO<sub>2</sub> ions for electron hole separate, effective photocatalysts by utilizing light energy to create e /h<sup>+</sup> pairs on the photocatalytic surface. The e/h<sup>+</sup> pairs are then available for oxidation and reduction processes, which usually involve the formation of reactive oxygen species, such as OH and O<sub>2</sub>, which then further aid in the decomposition of contaminants [16, 20].

Copper ferrite has tweaked the photocatalytic of the synthesized materials. It has good selectivity for the removal of organic pollutants from wastewater.

#### EXPERIMENTAL

#### Materials

Chemicals with high perfection were acquired from business sources (Aldrich) and utilized without further distillation. Deionized refined water was utilized for every one of the experiments. The raw materials are Ferric sulfate monohydrate (Fe<sub>2</sub>(SO<sub>4</sub>)3H<sub>2</sub>O, assay:99%), Copper(II)sulfate pentahydrate(CuSO<sub>4</sub>.5H<sub>2</sub>O), Ethanol, Ammonia, Polyvinylpyrrolidone (C<sub>6</sub>H<sub>9</sub>NO) n, assay:98%)

# Synthesis of PVP coated CuFe<sub>2</sub>O<sub>4</sub> nanoscale particles

The PVP coated copper ferrite nanoparticles have been synthesized by chemical co-precipitation route with simple manipulations. In this experiment, an aqueous solution containing 100ml is compiled regarding ferric sulfate, Copper (II) sulfate pentahydrate and Polyvinylpyrrolidone (PVP) were mixing due to Stoichiometric proportion. The Stoichiometric combinations had been stirred because of 45 min to gain a homogeneous solution yet after the required quantity of ammonia was once dissolved into 50 ml over distilled water. The solution was introduced carefully according to the combination because preserving the pH degree at 11. It is aged in accordance with enhancing their magnetic properties, controlled crystallite or crystallinity. The precipitates have been magnetically separated by the magnet bar. The separated nanoparticle was once dissolved into methanol and since once more were separated via magnet bar. This method was consistently repeated 4 times among order to except the extra amine molecules. We execute attain black powder of copper ferrite materialization permanency afterward drying the precipitate at a hot air oven because of 6hrs. The dried powder used to be saved at the furnace then annealed at 600°C because 4hrs, of the system to modify high crystallinity nanoscale particles.

#### **RESULTS AND DISCUSSION**

#### **Photocatalytic Activity Analysis**

The photocatalytic activity of copper ferrites materials were assessed by observing the photodegradation of methylene orange (MO) in the fluid arrangement, separately [21]. Basically, photo activation happens in the scope of 300–388 nm. [25, 26]. Evolution of the spectral changes taking place during the photodegradation of the MO under copper ferrites composition is shown in Fig.1.



Fig 1: UV-visible Absorption Spectra of Cufe<sub>2</sub>o<sub>4</sub> Ferrite Particles

MO was chosen as a result of its strong absorption to metal oxide surfaces, all around characterized optical absorption and great protection from light degradation. The photocatalytic tests were completed on bright days between 10 am and 1 pm at an open place. The 0.25 g of photocatalyst of pure and CuFe<sub>2</sub>O<sub>4</sub> ferrite was rushed into 100 ml of 10 mg/L MO watery arrangement, individually. The ferrite solutions were magnetically mixed for 30 min to achieve absorption desorption balance among MO dey and catalytic ferrite materials [15]. Natural light was used to illuminate the mixture. Then, after the arrangements were removed every 30 minutes (up to 90 minutes), the photocatalyst was immediately separated from the mixture arrangement by centrifugation, and the UV-Vis absorption of the cleaned-up arrangements was assessed using a UV-Vis spectrophotometer (Shimadzu, UV-1800). The MO arrangement's absorbance was calculated to be 626 nm, which corresponds to its maximum absorption wavelength. Fig. 1 displays the MO absorption spectra for various time intervals of 0, 30, 60, and 90 minutes employing a catalyst made of pure and ferrite materials, as a function of wavelength (400-800 nm). The absorption peak of MO, which is concentrated at 626 nm, was employed to characterize the deterioration impact. The figures clearly demonstrate that the most extreme absorption peak declines as light time increases. This shows that the MO dye concentration decreases when exposed to pure, catalytic ferrite materials and brighter sunlight. The homo and hetero-polyaromatic rings found in the dye particles were destroyed, or MO degraded quickly, as evidenced by the decline in the mixed collection's absorption, which is supported by the lower intensities of the MO absorbance peak [18, 20]. By altering the period from 0-90 minutes, the effect of pure and CuFe<sub>2</sub>O<sub>4</sub> ferrite catalysts on the percentage degradation of the MO dye has been investigated. For MO-catalyst solutions, the percentage degradation increases quickly with the passage of time. Using pure and catalytic ferrite materials, the greatest amount of MO dye

degradation that occurred in 90 minutes of sunshine exposure was 5% and 17%, respectively. For the MO solution, a steady decline in the strength of the strong absorption band at 426 nm was seen. The formation of heterostructure between MO and CuFe<sub>2</sub>O<sub>4</sub> ferrite spinel ferrite phase, which transfers photoinduced electrons or holes from one material with a higher CB minimum (lower VB maximum) to another with a lower CB minimum (lower VB maximum), is related to the improvement of photocatalytic efficiency. This can lead to an increase in separation and a decrease in internal recombination of photoinduced electrons or holes [18]. The higher specific surface area of samples containing CuFe<sub>2</sub>O<sub>4</sub> ferrite, which provides more accessible active sites for photocatalytic reaction, may be related to the samples' maximum activity.

## CONCLUSION

Copper ferrite is synthesized using a chemical co-precipitation process. In this study, methylene orange dye was successfully degraded by  $CuFe_2O_4$ . Due to the high absorption activity of  $CuFe_2O_4$  ferrite samples at 625nm wavelength by photocatalytic method, the surface of methylene orange dye is completely degraded.  $CuFe_2O_4$  provides more accessible active sites for the photocatalytic reaction. Thus, the photocatalytic use of  $CuFe_2O_4$  nanoparticles to remove organic contaminants from wastewater has been confirmed.

#### Acknowledgement

Authors are remaining grateful to the Administration of St. Joseph's College of Arts & Science (Autonomous), Cuddalore, Tamilnadu, India, for provided that the "Research Lab for Nanotechnology and Crystal growth" laboratory for synthesis of copper ferrite nanoparticles in this work.

# **Declaration of Competing Interest**

The authors affirm that they have no known financial or interpersonal conflicts that would have perceived to have an impact on the research presented in this study.

## **Ethical approval**

No one who wrote this article used either human or animal subjects in their research.

#### **Informed consent**

None

# Funding

The authors did not receive any funding from any of the agencies.

## Reference

- Hcini, S., Omri, A., Boudard, M. et al. J Mater Sci: Mater Electron (2018) 29: 6879. https:// doi.org/10.1007/s10854-018-8674-3
- 2. Kamellia Nejati, Rezvanh Zabihi.: Chemistry Central Journal 2012, 6:23 .https://doi. org/10.1186/1752-153X-6-23
- Chauhan J, Shrivastav N, Dugaya A, Pandey D (2017) Synthesis and Characterization of Ni and Cu Doped ZnO. J Nanomed Nanotechnol 8: 429. doi: 10.4172/2157-7439.1000429
- PratibhaRao,R.V.Godbole,Sunita Bhagwat.: Materials Chemistry and Physics171 (2016) 260-266, Copper doped nickel ferrite nanocrystalline thin films: A potential gas sensor towards reducing gases, http://dx.doi. org/10.1016/j.matchemphys.2016.01.016
- Mohd Hashim, M. Raghasudha, Jyoti Shah, Sagar E. Shirsath, D. Ravinder, Shalendra Kumar, Sher Singh Meena, Pramod Bhatt, Alimuddin, Ravi Kumar, R.K. Kotnala .:Journal of Physics and Chemistry of Solids (2017), DOI: 10.1016/j.jpcs.2017.08.022
- 6. P. Sivakumar et al Materials Research Bulletin, Prepar ation and properties of nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) nanoparticles via sol–gel auto-combustion method, Materials Research Bulletin 46 (2011) 2204–2207, doi:10.1016/j. materresbull.2011.09.010
- Lassoued, A., Lassoued, M.S., Karolak, F. et al. J Mater Sci: Mater Electron (2017) 28: 18480. https://doi.org/10.1007/s10854-017-7795-4

#### 20 R. Sagayaraj et al. / St. Joseph's Journal of Humanities and Science (Volume 9 Issue 2 August 2022) 15-21

- Raghvendra Singh Yadav et al Journal of Magnetism and Magnetic Materials, Effects of annealing temperature variation on the evolution of structural and magnetic properties of NiFe<sub>2</sub>O<sub>4</sub> nanoparticles synthesized by starch-assisted sol–gel auto-combustion method, Journal of Magnetism and Magnetic Materials 394 (2015) 439–447, http://dx.doi. org/10.1016/j.jmmm.2015.07.012
- 9. Gopathi Ravi Kumar et al Materials Sciences and Applications, Synthesis, Structural and Magnetic Properties of Copper Substituted Nickel Ferrites by Sol-Gel Method, Materials Sciences and Applications, 2012, 3, 87-91, http://dx.doi.org/10.4236/msa.2012.32013
- 10. Lall Beeharry Zakiyah et al Up-scalable synthesis of size-controlled copper ferrite nanocrystals by thermal treatment method, Materials Science in Semiconductor Processing 40 (2015) 564–569, http://dx.doi. org/10.1016/j.mssp.2015.07.027
- 11. Safia Anjum et al IEEE TRANSACTIONS ON MAGNETICS, Effect of Cu-Doped Nickel Ferrites on Structural, Magnetic, and Dielectric Properties, IEEE TRANSACTIONS ON MAGNETICS, VOL. 50, NO. 8, AUGUST 2014, DOI 10.1109/TMAG.2014.2318312
- Hongyu Wang et al J Mater Sci: Mater Electron, Synthesis and microwave absorbing properties of Ni–Cu ferrite/ MWCNTs composites, J Mater Sci: Mater Electron (2015) 26:7698– 7704, DOI 10.1007/s10854-015-3411-7
- H. S. Ahamad, N. S. Meshram, S. B. Bankar, S. J. Dhoble & K. G. Rewatkar (2017) Structural properties of Cu<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> nano ferrites prepared by urea-gel microwave auto combustion method, Ferroelectrics, 516:1, 67-73, DOI: 10.1080/00150193.2017.1362285
- 14. B.J. Madhu et al. / Materials Science and Engineering B 186 (2014) 1–6, http://dx.doi. org/10.1016/j.mseb.2014.02.018

- XUShihongetalPreparation and Photocatalytic Properties of Magnetically Separable Ti02 Supported on Nickel Ferrite, Chin. J. Chem. Eng., 132) 190-195 (2007). https://doi. org/10.1016/S1004-9541(07)60057-3
- 16. R. Cheng, X. Fan, M. Wang, M. Li, J. Tian and L. Zhang, RSC Adv., 2016, DOI: 10.1039/ C5RA27221A.
- 17. Shou-Qing Liu , Bo Xiao , Lian-Rong Feng, Shan-Shan Zhou , Zhi-Gang Chen , Cheng-Bao Liu , Feng Chen , Zheng-Ying Wu , Nan Xu , Won-Chun Oh , Ze-Da Meng, Graphene oxide enhances the Fenton-like photocatalytic activity of nickel ferrite for degradation of dyes under visible light irradiation, C a r b o n 6 4 (2013)197–206. https://doi.org/10.1016/j. carbon.2013.07.052
- Yuanzhi Hong, Ao Ren, Yinhua Jiang, Jinhua He, Lisong Xiao, Weidong Shi.: Ceramics International 41 (2015) 1477– 1486, http:// dx.doi.org/10.1016/j.ceramint.2014.09.082
- Sagayaraj, R., Aravazhi, S. & Chandrasekaran, G. J Supercond Nov Magn (2018) 31: 3379. https://doi.org/10.1007/s10948-018-4593-z
- 20. Erik Casbeer , Virender K. Sharma , Xiang-Zhong Li.: Separation and Purification Technology 87 (2012) 1–14, doi: 10.1016/j. seppur.2011.11.034
- 21. N. Baliarsingh, K. M. Parida, and G. C. Pradhan .:Ind. Eng. Chem. Res., 2014, 53 (10), pp 3834–3841, DOI: 10.1021/ie403769b
- 22. Veinger, A.I., Zabrodskii, A.G., Tisnek, T.V. et al. Semiconductors (2004) 38: 782. https:// doi.org/10.1134/1.1777600
- 23. BO XIAO and SHOU-QING LIU, Enhancing the Photocatalytic Activity of Nickel Ferrite Doped with Graphene, Asian Journal of Chemistry; Vol. 26, No. 5 (2014), 1391-1393, http://dx.doi.org/10.14233/ ajchem.2014.17239

R. Sagayaraj et al. / St. Joseph's Journal of Humanities and Science (Volume 9 Issue 2 August 2022) 15-21 21

- 24. Rimi Sharma, S. Bansal and SonalSinghal.: RSC Adv., 2015,5, 6006-6018 . DOI:10.1039/ C4RA13692F
- Alina M. Balu, Babita Baruwati, Elena Serrano, Jaume Cot, Javier Garcia-Martinez, Rajender S. Varma and Rafael Luque.: Green Chem., 2011, 13, 2750, DOI: 10.1039/c1gc15692f
- 26. Song Sun, Xiaoyan Yang, Yi Zhang, Fan Zhang, Jianjun Ding, Jun Bao, Chen Gao, Enhanced photocatalytic activity of s p o n g e 1 i k e  $ZnFe_2O_4$  synthesized by solution combustion method, Progress in Natural Science: Materials International 2012;22(6):639–643, http://dx.doi.org/10.1016/j.pnsc.2012.11.008